

CHARACTERIZATION OF SHOCK EFFECTS IN CALCITE BY RAMAN SPECTROSCOPY: RESULTS OF EXPERIMENTS. M. S. Bell¹, ¹ Jacobs@NASA/Johnson Space Center, Houston, TX, mary.s.bell@nasa.gov.

Introduction: Carbonates comprise ~20% by volume of present day Earth's sedimentary rocks and store most of the terrestrial CO₂ inventory [1]. Some of the oldest meta-sedimentary rocks found on Earth contain abundant carbonate from which impact-induced release of CO₂ could have played a role in the formation and evolution of the atmosphere [2]. Carbonates are also present in the target materials for ~30% of all terrestrial impact structures [3,4,5] including large impacts such as Chicxulub which happened to occur at a location with extraordinarily thick platform carbonate 3-6 km deep [6]. The impact release of CO₂ from carbonates can cause global warming as a result of the well-known greenhouse effect [7] and have subsequent effects on climate and biota [8,9]. Therefore, the shock behavior of calcite is important in understanding the Cretaceous-Paleogene event and other impacts with carbonate-bearing sediments in their target(s) such as Mars [10] and some asteroids [11]. A comprehensive survey utilizing a variety of techniques to characterize the effects manifest in Calcite (Iceland Spar) experimentally shocked to 60.8 GPa has been completed [12]. Results of analysis by Raman Spectroscopy are reported here.

Methods: Optical quality, single crystal Iceland spar (initial density ~2.719 gm/cm³) was chosen for the shock experiments to minimize shock effects caused by porosity and compositional heterogeneity in the sample. The disks were then ground flat, polished, and encased in metal holders as described by [13]. Shock waves were induced in the samples by impacting the target with 2.54 mm thick flyer plates at ambient temperatures. Projectiles were launched using the 20 mm-diameter propellant gun in the Johnson Space Center (JSC) Experimental Impact Laboratory to velocities in the range of 1.3 to 1.8 km/sec according to the methods of [14] to produce peak shock pressures in the target ranging from 9.0 to 60.8 GPa. The metal capsules that contained the cylindrical target discs were carefully machined open upon recovery and the shocked material was removed. The shocked samples consisted of loose friable masses. Recovered materials were sieved to the size fraction 50 to 150 μm for Raman analysis with comparison to an unshocked reference sample.

Raman spectra were collected at the NASA/Johnson Space Center using a Jobin-Yvon LabRAM HR800. The spectrometer was equipped with an argon ion (Ar⁺) gas laser and calibration was

done using the 520.3 cm⁻¹ plasma line of that laser. Laser power was 200 mW at the sample to maximize spectral quality as beam damage to the sample was not a concern. The slit width was set at 100 μm and a data collection interval of 1 cm⁻¹ was used in recording Raman spectra. Only Stokes lines were recorded. Data were recorded using a liquid-nitrogen-cooled charge coupled device (CCD) detector and the laser light was focused to a spot size of 1 μm on the surface through a microscope objective of 100x magnification. Spectral resolution is 4-5 cm⁻¹.

Raman Spectral Analysis: Raman data gives information about the behavior of the carbonate bonds and the pressure dependence of the vibrational spectra of carbonates may be used to infer the role of different structural units in their compaction [15]. In addition, phase transitions in carbonates are readily recognizable using the Raman technique [e.g. 16,17]. Clear, inclusion – free minerals such as optical quality Iceland spar present few problems with respect to the Raman technique because most of the beam energy is transmitted through the sample [18]. The observed frequencies of Raman spectra for unshocked Iceland spar agree well with previous single-crystal spectroscopic experiments [19,20,21,22,23] although literature values do show significant variation [22]. The Raman spectra of calcite includes two lattice modes T and L (translation and libration, respectively) below 300 cm⁻¹, the ν₄ (O-C-O in-plane bending) mode of the carbonate ion near 713 cm⁻¹, the ν₁ (C-O symmetric stretch) mode at 1086 cm⁻¹, the ν₃ (C-O antisymmetric stretch) mode near 1436 cm⁻¹, and the 2 x ν₂ (O-C-O out-of-plane bend) mode near 1750 cm⁻¹ [see 24 for more detailed descriptions]. The spectral range between 100 and 1800 cm⁻¹ acquired here encompasses these characteristic Raman vibrations. The Raman spectra of shocked samples show sharp Raman peaks for all experimental pressures. All of the Raman spectral bands are those of calcite and no spectral evidence can be seen for the formation of CaO, which should produce a strong Raman band at 360 cm⁻¹, or for amorphous material.

Frequencies of Raman band positions for the internal modes are not appreciably shifted to higher frequencies and show no systematic variation with shock pressure. In this study, all Raman bands shift from only 2 cm⁻¹ to less than 4 cm⁻¹. However, the libration lattice mode at 270 to 345 cm⁻¹ shows a good pressure dependent correlation for band shifting to higher frequency (R = 0.84). The only vibrational mode to show

appreciable peak broadening with increasing shock pressure is the $2 \times \nu_2$ (O-C-O out-of-plane bend) internal mode ($R = 0.607$). A variation of peak FWHM up to 2.7 cm^{-1} is seen in the spectra for this peak. All other R values for these data are <0.24 although the lattice mode spectral bands show more broadening than the internal mode spectral bands.

The only Raman data which show a systematic change with increasing shock pressure is related to a change in peak intensity and is plotted in Figure 1. The T and L lattice mode spectral bands have the greatest pressure dependent intensity loss diminishing to 34.34% and 23.29%, respectively, in samples shocked to 60.8 GPa. The spectral bands for the ν_4 and ν_1 internal modes decrease to 33.96% and 32.2% of their unshocked intensity at 60.8 GPa. In contrast, the other two internal modes, ν_3 and $2 \times \nu_2$, retain 68 to 84% of their unshocked intensity up to 60.8 GPa. The change in Raman peak intensity with increasing shock pressure is telling. There are two alternatives – either the laser beam is interrogating a smaller volume, or the volume is gaining an amorphous fraction that does not generate strong peaks. Additional peaks should develop in Raman spectra along with an increase in background intensity if there were amorphous material present. That means the laser beam is interacting with a diminishing crystallite volume. The Iceland Spar is becoming more translucent (less transmissive) as the grain size diminishes, scattering the beam and decreasing the effective beam interaction volume.

Conclusions: Except for the frequency shift of the L lattice mode associated with a change in the bonding environment between Ca^{2+} and the carbonate ion, these Raman spectral measurements of Iceland spar shock loaded to 60.8 GPa show no appreciable pressure dependent Raman frequency shifting or band broadening associated with internal CO_3^{2-} vibrations. This is consistent with the assessment of Kraft *et al.* (1991) that the carbonate group is relatively insensitive to pressure up to 60 GPa, with the dominant compaction mechanism being compression of the calcium polyhedra although it is unclear why the T lattice mode frequency was not shifted similarly to the L lattice mode as is the case reported by Kraft *et al.* (1991) for aragonite and dolomite. This work supports the conclusions of Pierazzo *et al.*, 1998 who posit that sulfur and water may have produced the more climatically active gasses injected into the stratosphere as a result of the Chicxulub Cretaceous/Paleogene impact event rather than CO_2 from the devolatilization of carbonates in the target.

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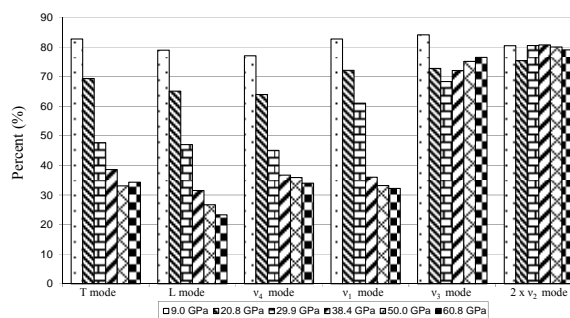


Figure 1: Raman average peak intensities relative to unshocked sample (100%) for shocked Iceland spar. Raman vibration modes are labeled as follows: T = translation, L = libration, ν_4 = internal in-plane bend, ν_1 = internal symmetric stretch, ν_3 = internal antisymmetric stretch, and $2 \times \nu_2$ = internal out-of-plane bend.